



# Dynamic observation of the diffusion layer in anodic processes of the Fe/H<sub>2</sub>SO<sub>4</sub> system with digital holography

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## ABSTRACT

The anodic dissolution mechanisms of the Fe/H<sub>2</sub>SO<sub>4</sub> system are complicated and controversial among different models. The main discrepancy concerns the composition and the structure of the films on the iron electrode during reactions. In the present study, the dynamic changes of the diffusion layer during the electrodisso- lution of iron in 0.5 mol·dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution are visually presented through the phase maps obtained by digital holography, which yields new information of anodic processes of the Fe/H<sub>2</sub>SO<sub>4</sub> system. It is deduced that the SO<sub>4</sub><sup>2-</sup> ions are transported from the bulk solution to the vicinity of the electrode and that crystalline precipitation of FeSO<sub>4</sub>·7H<sub>2</sub>O is formed and precipitated continuously within the late active and the limiting current region. These findings have led to the proposal of a model of the anodic dissolution of iron in H<sub>2</sub>SO<sub>4</sub> solution.

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## 1. Introduction

The anodic dissolution processes of iron in the sulfuric acid solution have been extensively studied as one of the typical nonlinear phenomena in electrochemistry [1–28]. The formation and the dissolution of surface films at Fe/H<sub>2</sub>SO<sub>4</sub> interface play an important role in the potentiostatic current oscillations. However, there have been two different opinions concerning the composition of the prepassivating film: some believed that the film is ferrous sulfate [1,6,9–12,14,17–20, 24,26], while others favored that it is ferrous oxide/hydroxide [2–5, 8,13,15,16,22,23,25,27,28]. Thus, the mechanisms of the Fe/H<sub>2</sub>SO<sub>4</sub> system are controversial among different models. Up to the present, the long standing issue remains unsettled [21–28]. The proposed reasons are that the surface film experiences dynamic changes during anodic processes of iron, and that no technique can detect the changes in the composition and the structure of surface film in real time.

It is clear that the transport of the electrolyte components plays an important role in the complicated mechanisms in the Fe/H<sub>2</sub>SO<sub>4</sub> system. The film formation is closely related with the component and the concentration of the electrolytes in the diffusion layer, whose dynamic changes become significant and informative to the understanding of the surface film. However, no satisfactory information about the dynamic behavior of the diffusion layer is available. In our recent work, digital holography was used to study the anodic dissolution of copper in NaCl solutions and was proved to be effective in

obtaining the dynamic changes in the diffusion layer at the electrode/electrolyte interface [29,30]. The phase difference of the object beam is directly proportional to the refractive index change inside the cell, which is brought about by the concentration changes of the soluble species in solution. Therefore, the dynamic behavior of the diffusion layer can be visually presented by the obtained phase difference [29,30] or refractive index change [28,31] to verify the occurrence of electrochemical reactions and identify reaction mechanisms.

The present study employs digital holography to investigate the iron electrodisso- lution in 0.5 mol·dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution. The dynamic changes of the diffusion layer during the anodic processes are obtained by the numerical reconstruction of the holograms. The formation and the composition of the surface film, vital to the revelation of the mechanism of anodic dissolution of iron electrode in sulfuric acid, are deduced via the cyclic voltammogram and the dynamic changes of the diffusion layer based on the phase difference data. This study proposes a model to explain the mechanisms of the anodic dissolution processes of iron in H<sub>2</sub>SO<sub>4</sub> solution.

## 2. Experimental

### 2.1. Electrochemical system

A stationary iron electrode (Puratronic, Alfa Aesar, 99.99%) with a diameter of 2 mm was used as the working electrode. The sample was sealed by a thin layer of epoxy resin, leaving only the end of the rod exposed to the solution. A large sheet of platinum was used as the counter electrode. The reference electrode was a saturated

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calomel electrode (SCE) with a Luggin capillary tip set at 1 mm from the surface of the working electrode. All potentials reported here were with respect to SCE. Before each experiment, the iron electrode was mechanically abraded with #1500 and #3000 emery papers to a mirror-like surface and then cleaned by alcohol and distilled water in an ultrasonic bath. The electrolyte,  $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$  solution, was prepared with triply distilled water and analytical grade chemicals. The voltammetric measurements were performed by means of the CHI 660B electrochemical station at room temperature under non-deaerated condition.

## 2.2. Holographic system

The experimental setup of holography is referred to [30]. The refractive index variation of solution caused by the concentration changes anywhere inside the electrochemical cell led to the phase changes of the object wave, which were finally recorded in the holograms. The holograms were recorded by a digital camera and processed by a personal computer. During the hologram processing processes, the phase changes were reconstructed from the AVI video signals by software developed with MATLAB® (copyright by The Mathworks, Inc.) [30]. The distributions of the phase difference

between the initial and any other time points can be continually displayed on the PC monitor at 25 frames per second.

## 3. Results and discussion

The cyclic voltammogram at the potential scan rate of  $10 \text{ mV} \cdot \text{s}^{-1}$  in the system of  $\text{Fe}/0.5 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$  solution is shown in Fig. 1 (top). It can be roughly divided into four regions: (I) the active region, (II) the limiting current region (LCR), (III) the oscillatory region and (IV) the passive region. The iron electrode dissolves anodically in the active region. The LCR (the plateau region) is observed at the equal rates for the formation and the dissolution of the surface film. The current drops to almost zero for the passive films are formed on the electrode.

Fig. 1 (bottom) presents reconstructed phase maps at the given time points during the dynamic processes of anodic polarization of iron. In each phase map, the left is the electrode, the right is the solution, while in between is the interface. The position of the electrode surface is sketched in Fig. 1a. The maps indicate local variations in the refractive index of the electrolyte, which correlate with the concentration of dissolved species. The phase differences  $\Delta\phi$  appear only at the interface, where  $\Delta\phi > 0$  means the increase of the

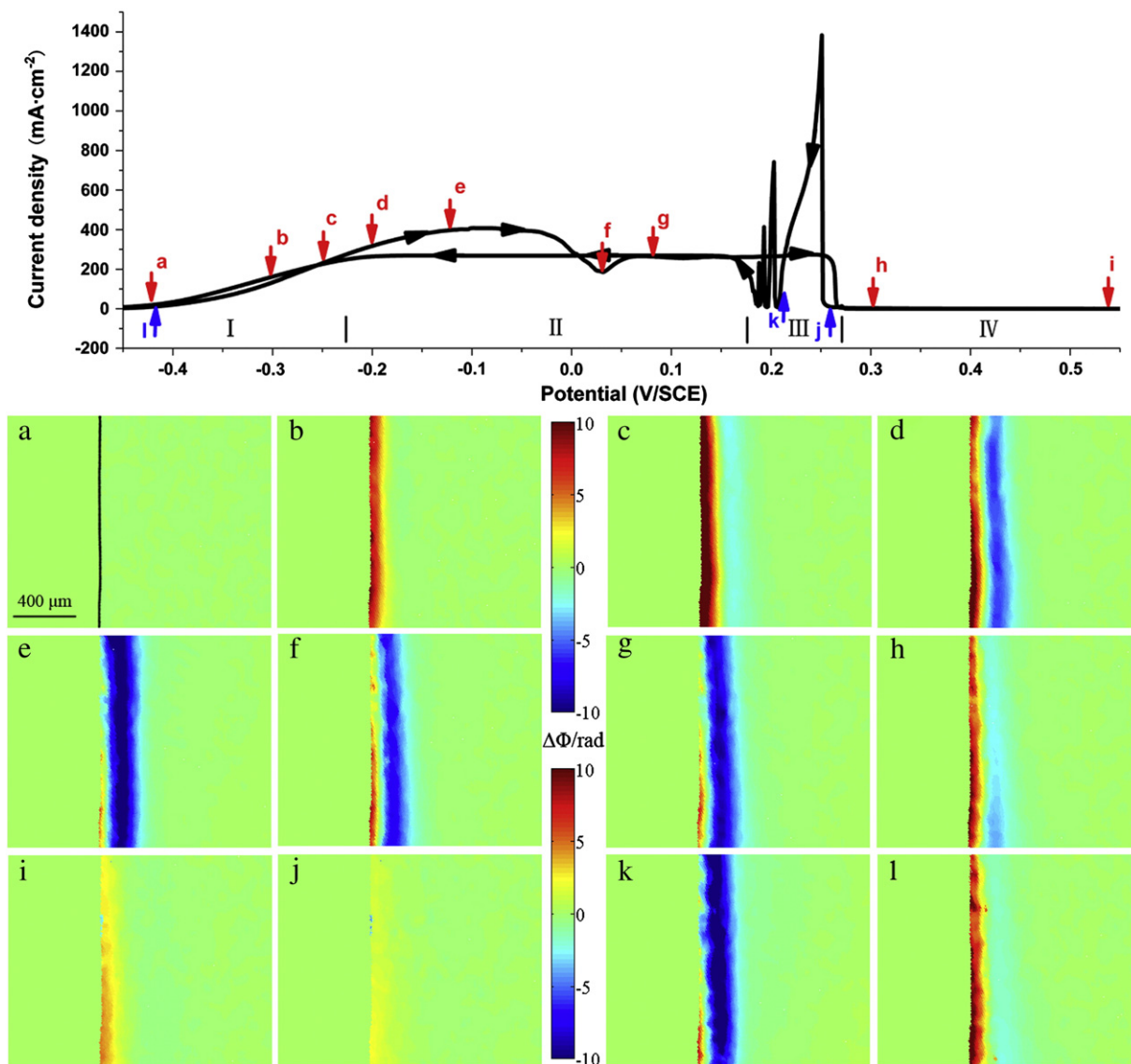


Fig. 1. The cyclic voltammogram of the  $\text{Fe}/0.5 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$  system with the scan rate of  $10 \text{ mV} \cdot \text{s}^{-1}$  and the corresponding phase maps at different times.

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